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A review on adsorption working pairs for refrigeration

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Abstract

Solid sorption refrigeration is a type of environmental benign and energy saving technology and the sorbents utilized can be divided into physical, chemical and composite sorbents, according to the nature of the forces involved in the adsorption process. The types, characteristics, advantages and disadvantages of different adsorbents, refrigerants and working pairs are summarized in this paper, together with the models that describe the adsorption equilibrium. Moreover, some of the procedures to prepare composite adsorbents are presented. The application of different working pairs for different situations is related with the adsorption heat, the adaptability to the driving temperature and to the desired working pressure. The methods to measure the adsorption quantity of different working pairs are compared, and future research directions of adsorption working pairs are also analyzed.

Keywords: Adsorption refrigeration; Working pair; Adsorbent; Refrigerant

Contents

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1. Introduction

Adsorption[1] refrigeration systems, which can be powered by low-grade heat and utilizes refrigerants with zero ODP and GWP, received increased attention since the 1990s [1–3]. Compared with absorption refrigeration, which can also be powered by low-grade heat, the advantages of solid sorption refrigeration are as follows:

(1) Solid sorption systems can be powered by sources with wide temperature range. Temperature as low as 50 °C can be used as heat source for adsorption systems, but in absorption systems the source should be at least at 70 °C, even if two-stage cycle is adopted. Heat sources with temperature close to 500 °C can be used directly in adsorption without producing any kind of corrosion problem, while in absorption systems, severe corrosion would start to occur for temperatures above 200 °C.
(2) Adsorption refrigeration systems are suitable for conditions with serious vibration, such as in fishing boats and locomotives [4,5], but absorption systems, due to the fact that the absorbent is in liquid state, have problems because the absorbent can flow from the generator to the evaporator or from the absorber to the condenser. When such a displacement of the absorbent occurs, the refrigerant became polluted and the system cannot work normally.
(3) Adsorption systems can be much simpler than absorption systems. For example, in the NH_3–H_2O absorption system, dephlegmate equipments must be coupled to the system because the boiling point of water is similar to that of ammonia.

The adsorption process is divided into physical adsorption [6–8] and chemical adsorption [9–11]. Physical adsorption is caused by van de Walls force between the molecules [12] of the adsorbent and the adsorbate. Physical adsorbents with mesopores can adsorb consecutives layers of adsorbate, while those with micropores, have the volume of the pores filled with the adsorbate. Physical adsorbents develop the selectivity to the adsorbate after the former undergo specific treatments, like react under a gas stream or with certain agents. The kind of treatment will depend on the type of sorbents [13].

Chemical adsorption is caused by the reaction between adsorbates and the surface molecules of adsorbents. Electron transfer, atom rearrangement and fracture or formation of chemical bond always occurs in the process of chemical adsorption [14]. Only one layer of adsorbate reacts with the surface molecules of chemical adsorbent. The adsorbate and adsorbent molecules after adsorption never keep their original state, e.g., complexation occurs between chlorides and ammonia. Moreover, there are the phenomena of salt swelling and agglomeration, which are critical to heat and mass transfer performance.

Composite adsorbents [15–17] started to be studied about 20 years ago [18], and they aimed to improve the heat and mass transfer performance of the original chemical adsorbents [16,19,20]. This kind of adsorbent is usually obtained by the combination of a chemical adsorbent and a porous medium, that can be or not a physical adsorbent, such as activated carbon, graphite, carbon fibre, etc. [16,21,22].

2. Adsorbents

2.1. Physical adsorbents

The common physical adsorbents for adsorption refrigeration are activated carbon, activated carbon fibre, silica gel and zeolite.

2.1.1. Activated carbon and activated carbon fibre

The activated carbon is made of materials such as wood, peat, coal, fossil oil, chark, bone, coconut shell and nut stone. The structure of activated carbon is shown in Fig. 1. The microcrystal for the activated carbon produced from bone is a six element carboatomic ring [13], and the adsorption performance is influenced by the functional groups that is connected to the carboatomic ring. For example, arene group increases adsorption, while sulfonic group decreases it. Acidic functional group increases adsorption selectivity. The functional groups on the surface of activated carbon are different if the original carbonaceous material and the activation method are different. The specific area of activated carbon is between 500 and 1500 m^2/g.

[1] Although some authors use the term absorption as a synonymous not only for liquid sorption but also for chemisorption. In the present text, absorption is used only as a synonymous for liquid sorption, and adsorption is used as a synonymous for solid sorption (both physical and chemical).

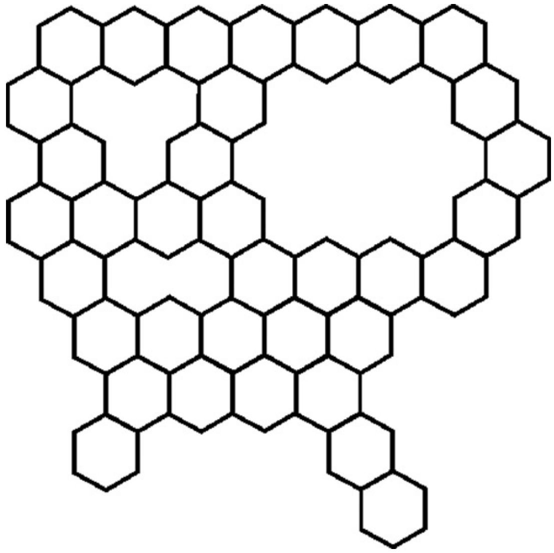

Fig. 1. Structure of activated carbon [13].

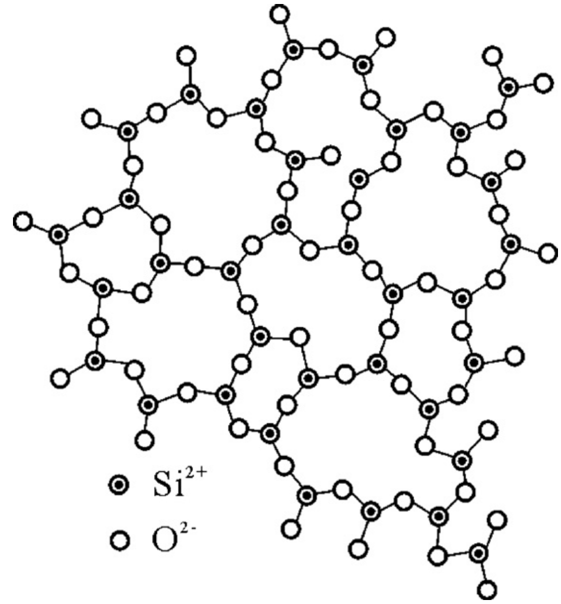

Fig. 2. Array of SiO_4 in silica gel [23].

The net structure of activated carbon pores is composed of irregular channels, which have larger pore area at the surface of the grain, and narrow pore area within the grain [23]. The difference between activated carbon and other types of adsorbent is the surface feature. The whole surface of activated carbon is covered by an oxide matrix and by some inorganic materials, and therefore, it is non-polar or has a weak polarity. The adsorption heat of activated carbon pairs is lower than that of other types of physical adsorbent pairs.

Activated carbon fibre is generally used in the production of fabric, such as cloth, tissue, etc. Compared with granular activated carbon, carbon fibre has better mass transfer performance. The specific surface area of activated carbon fibres is larger than that of activated carbon, the pores of activated carbon fibre are more uniform than that of activated carbon, and the heat transfer performance of activated carbon fibres is also larger than that of activated carbon [24]. The disadvantages of activated carbon fibres are the anisotropic thermal conductivity, and the higher contact thermal resistance between the fibre and the adsorber wall, when compared with granular activated carbon.

2.1.2. Silica gel

The silica gel is a type of amorphous synthetic silica. It is a rigid, continuous net of colloidal silica (Fig. 2), connected to very small grains of hydrated SiO_4 [23]. The hydroxyl in the structure is the adsorption center because it is polar and can form hydrogen bonds with polar oxides, such as water and alcohol. The adsorption ability of silica gel increases when the polarity increases. One hydroxyl can adsorb one molecule of water.

Each kind of silica gel has only one type of pore, which usually is confined in narrow channels. The pore diameters of common silica gel are 2, 3 nm (A type) and 0.7 nm (B type), and the specific surface area is about 100–1000 m^2/g. Silica gel is widely used for desiccation because of its large adsorption ability. Type A silica gel could be used for all desiccation conditions, but type B silica gel can only be used when the relative humidity is higher than 50%.

2.1.3. Zeolite

Zeolite is a type of aluminasilicate crystal composed of alkali or alkali soil. The chemical formula of zeolite is

$$M_{y/n}[(AlO_2)_y(SiO_2)_m]zH_2O \tag{1}$$

where y and m are all integers and m/y is equal or larger than 1. n is the chemical valence of positive ion of M, z is the number of water molecule inside a crystal cell unit.

A crystal cell unit of zeolite is shown in Fig. 3. The positive ion must have its electric charge balanced with the electric charge of aluminium atom. The net electric charge of each aluminium atom is -1. Water can be removed by heating. The porosity of the aluminasilicate skeletal is between 0.2 and 0.5. The aluminasilicate skeleton has a cage format, and it is usually connected by six casement sections, which can adsorb a large amount of extra molecules [23].

There are about 40 types of natural zeolites, and the main types for adsorption refrigeration are chabazite, sodium

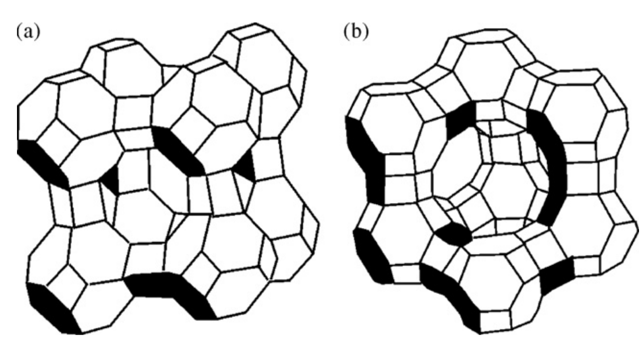

Fig. 3. Crystal cell unit of zeolite: (a) crystal cell unit of type A zeolite; (b) crystal cell unit of type X, Y zeolite or faujasite [23].

chabazite, cowlesite and faujasite. About 150 types of zeolites can be artificially synthesized, and they are named by one letter or a group of letters, such as type A, type X, type Y, type ZSM, etc. [13].

Artificially synthesized zeolites are more expensive than natural zeolites, but they have higher bulk specific weight and better heat transfer performance. The adsorption ability of zeolites is related to the proportion between Si and Al, and the adsorption ability is higher when this proportion is small.

The pore size of zeolites determines the selectivity for different adsorbates, and the cage structure of the micropore makes that the adsorption process could proceed in a small range, thus the zeolites are also named as zeolite molecular sieve. Artificially synthesized zeolite molecular sieves have micropores with uniform size, and different sizes can be obtained by different manufacturing methods. 4A, 5A, 10X and 13X zeolite molecular sieves are the main types used for adsorption refrigeration. The adsorption and desorption heat of zeolite pairs are high, and the desorption temperature of these pairs is also high, and about 250–300 °C. Most zeolite molecular sieves can be destructed at temperatures higher than 600–700 °C, however mercerized zeolites can withstand temperatures of 800 °C. The zeolites are usually employed in adsorption air conditioner systems that have heat source between 200 and 300 °C.

2.2. Chemical adsorbents

Chemical adsorbents mainly include metal chlorides, metal hydrides and metal oxides.

2.2.1. Metal chlorides

The metal chlorides for adsorption refrigeration are mainly calcium chloride, strontium chloride, magnesium chloride and barium chloride [25]. The adsorption reaction between metal chlorides and refrigerants is a complexation reaction, and the complex compound is also called coordinated compound [26].

The coordinated compound is different if the element located in different period of chemical elements. According to the theory of coordinate bond, the center atom provides a free hybrid orbit for a lone electron pair, which is provided by a ligand, to form a coordinate bond. For chemical elements in the second period, for example, Li(I), Be(II), B(III), the valence electron layer has four free orbits, which are 2s, $2p_x$, $2p_y$ and $2p_z$, and they could form three types of hybrid orbits, which are line type (sp hybrid orbit), plane triangle type (sp^2 hybrid orbit) or regular tetrahedron (sp^3 hybrid orbit). The adsorbents for adsorption refrigeration, such as K(I), Rb(I), Cs(I), Ca(II), Sr(II), are mainly the elements in the fourth, fifth and sixth periods, and the reaction between adsorbents and adsorbates are more complex because they are transition metals. For these metal chlorides, which have a regular dodecahedron structure, the sp^3d^4 hybrid orbit can occur [27].

Ammonia is the usual adsorbate of metal chlorides. During the adsorption process, salt swelling and agglomeration can occur and influence the heat and mass transfer performance.

2.2.2. Salt and metal hydrides

Hydrogen can react with almost all elements, and forms four types of hydrides. The first type is composed by salt hydrides, such as LiH and CaH_2, and which can be formed by the reaction between hydrogen and the elements of IA and IIA subgroup, due to their low electro-negativity and high chemical activity. Metal hydrides are the second type of hydrides. Hydrogen atom enters the crystal lattice of a parent metal when it reacts with transition metals, and forms metal hydrides. The other types of hydrides are the covalent high-polymerized hydrides, and the non-metal molecular hydrides.

Salt hydrides and metal hydrides can be utilized for adsorption refrigeration. The salt hydrides have hexagonal crystal lattice structure with large density. In the adsorption process, H atoms become protons when they enter the space between hexagonal crystal lattices. The electron motion is similar to the electron motion of metal bonds.

Hydrides with special structure appear when the quantity of hydrogen available for reaction increases too much. The density of salt hydrides are larger than the density of simple metals, but the density of metal hydrides is smaller than the density of simple metals because the volume and the mass of the former type does not increase proportionally in the adsorption process [28].

2.2.3. Metal oxides

The metal oxides are usually employed as catalyst for oxidation and deoxidation reactions. When the metal oxides are used as adsorbents in adsorption heat pump [11,29,30], oxygen is the refrigerant. On the surface of metal oxides, the elements which influence the adsorption performance are the coordination number of the metal ion, the unsaturated degree of coordination, the direction of the chemical bond on the surface of the chemical material, the symmetrical characteristic of the transition metal ligand field, the number of d electrons of the transition metal ligand field, and the arrangement of the active centers [31].

The swelling and agglomeration also occur during the adsorption in metal oxides.

2.3. Composite adsorbents

Composite adsorbents are developed and studied with mainly two goals:

(1) Improve heat and mass transfer performance of chemical adsorbents [32], specially due to the swelling and agglomeration phenomena. Salt swelling reduces the heat transfer, and salt agglomeration reduces the mass transfer. Therefore, the additive for chemical adsorbents must have a porous structure and high thermal conductivity, such as expanded graphite, to help avoiding the above-mentioned problems [33,34].
(2) Increase the adsorption quantity of physical adsorbents [35]. The addition of chemical sorbents in the physical sorbents increases the adsorption capacity of the latter, without resulting in the problems found in the former.

Table 1
Some physical properties of common refrigerants for adsorption systems

Refrigerants	Chemical formula	Normal boiling point (°C)	Molecular weight	Latent heat of vaporization L (kJ/kg)	Density ρ (kg/m^3)	$\rho \times L$ (MJ/m^3)
Ammonia	NH_3	−34	17	1368	681	932
Water	H_2O	100	18	2258	958	2163
Methanol	CH_3OH	65	32	1102	791	872
Ethanol	C_2H_5OH	79	46	842	789	665

The composite adsorbents made from porous media and chemical sorbents are commonly a combination of metal chlorides and activated carbon, or activated carbon fibre, or expanded graphite, or silica gel or zeolite.

The methods to produce composite adsorbents are mainly as follows:

(1) *Simple mixture*: In such a process, the chemical adsorbent and the additive are mixed in a defined mass or volume ratio. Such a type of method is mainly used when the additive is granular, like activated carbon [15,16].
(2) *Impregnation*: This method is mainly used for activated carbon fibre, graphite fibre or expanded graphite. In this method, the chemical adsorbent is first dissolved in the water or other solvent. Then, the additive is put in the solution, and dried to remove the solvent. One advantage of such a type of adsorbent is the large porosity, which benefits the refrigerant mass transfer. Such a type of adsorbent can have high thermal conductivity in the longitudinal direction, if carbon fibre is the additive. The disadvantage in using carbon fibre is the poor thermal conductivity in the fibres radial direction and the high thermal resistance between the fibre and reactor wall. The thermal resistance can become even larger if the composite adsorbent swells during adsorption [36,37].
(3) *Mixture or impregnation and consolidation*: Consolidated adsorbent can be produced by compressing the composite powder prepared by mixture or impregnation, as explained above, or by first compressing the additive or the physical sorbent, and then, impregnating it with the salt solution, with posterior drying to remove the solvent. The advantage of such a type of adsorbent is the high thermal conductivity in the direction perpendicular to the compression, and the disadvantage is related to the number of operation necessary to achieve the final compound. The mass transfer performance is seriously influenced by the ratio between the components and bulk density, therefore these parameters must be carefully chosen [16,38].

3. Refrigerants

3.1. Most common refrigerants

Adsorption technology can be used not only for air conditioning and refrigeration but also to upgrade heat with thermal transformers, and the type of refrigerant should be selected according to the application.

The requirements for a suitable refrigerant are generally as follows: (1) high latent heat of vaporization per volume unit or mass unit, (2) thermal stability, (3) environmental harmless, (4) nonflammable, (5) innoxious, (6) saturation pressure between 1 and 5 atm in the working temperatures (a perfect value would be close to 1 atm). Unfortunately, there are no refrigerants that have all the characteristics above, and the common refrigerants for adsorption refrigeration system are ammonia, water and methanol. Some physical properties of refrigerants for adsorption systems are shown in Table 1.

Refrigerants with boiling point below −10 °C at 1 atm are positive pressure refrigerants, whereas the other ones are vacuum refrigerants. Ammonia is an example of positive pressure refrigerant, and it can be used with chlorides, activated carbon and activated carbon fibre. The saturation pressure of ethanol and methanol [39] are similar, but the latent heat of the former is about 30% lower than that of latter [40]. Methanol is normally used in association with activated carbon or activated carbon fibre. Water could be considered as a perfect refrigerant, except for its extreme low saturation pressure and for the impossibility to produce temperatures below 0 °C. Water is normally employed in pair with silica gel or zeolite.

3.2. Other refrigerants

Hydrogen and oxygen are examples of other refrigerants that can be adopted in adsorption refrigeration systems.

Hydrides are the adsorbents for hydrogen, which is produced from the decomposition of water, and it is inflammable, explosive and requires extremely precaution to be handled.

The types of oxygen that can be adsorbed by oxides are O_2, O_2^-, O^- and O^{2-}. The reaction between oxides and oxygen has large enthalpy, thus, it is usually employed in chemical heat pumps [31,41,42]. However, this pair is also suitable for cryogenic system with temperatures below 120 K.

Other refrigerants, as R134a, R22, R407c and ethanol can be utilized if activated carbon or activated carbon fibre is the sorbent. However, compared with methanol, their mass unit cooling power is smaller due to their small adsorption quantity or due to their low latent heat of vaporization. Besides the limitations described above, HCFCs and HFCs are also not recommended because of their relative high GWP values [43,44].

4. Equilibrium adsorption models

The equilibrium adsorption quantity is the amount of refrigerant adsorbed by the sorbent when the reaction time

tends toward infinite, and it is an important parameter for adsorption working pairs. The equilibrium adsorption models for physical adsorption and chemical adsorption are different. The equilibrium in physical adsorption is divariant, and the model includes the influence of the pressure and temperature, while equilibrium in chemical adsorption is monovariant, and only one parameter (temperature or pressure) is necessary [45].

4.1. Equilibrium models for physical adsorption

The equilibrium model for physical adsorption is a function of adsorbent temperature and pressure, and it is written in a generic form as

$$x_\infty = f(p, T) \tag{2}$$

Models with different fixed parameters are as follows:

$$x_\infty = f(p)_T \quad \text{isothermal} \tag{3}$$

$$x_\infty = f(T)_p \quad \text{isobaric} \tag{4}$$

$$p = f(T)_x \quad \text{isosteric} \tag{5}$$

Adsorption isotherm models are utilized only to fit data from micro-adsorption quantity measurements because the isothermal condition cannot be achieved if the adsorption quantity is larger and therefore, heat production from the adsorption reaction is also larger. Adsorption isobar models are more suitable to design adsorption refrigeration system because the amount desorbed and adsorbed during a cycle can be easily calculated. Adsorption isosteric models are convenient to calculate the adsorption heat and usually utilized for the working pair selection.

Equilibrium adsorption curves for physical adsorption are shown in Fig. 4, where P_e is the evaporating pressure and P_c is condensing pressure. Fig. 4 shows that the adsorption quantity is influenced by two parameters, i.e. temperature and pressure [46–48].

The equilibrium adsorption/desorption quantity of physical adsorption in micropores is usually calculated by the Dubinin–Astakhov (D–A) equations [49,50], which are [49–51]:

$$x = x_0 \exp\left[-k\left(\frac{T}{T_s} - 1\right)^n\right] \tag{6}$$

or

$$x = x_0 \exp\left[-D\left(T \ln\frac{P_s}{P}\right)^n\right] \tag{7}$$

where x_0, k, D and n are coefficients, which are different not only for different working pairs, but also different for the same working pair, according to the brand and type of the adsorbent, T is adsorption temperature (K), T_s is the saturated temperature of refrigerant (K), P_s is the saturated pressure of refrigerant (Pa), P is the pressure of the system (Pa) and x is the adsorption quantity of refrigerant in the adsorbent (kg/kg).

4.2. Equilibrium models for chemical adsorption

The equilibrium adsorption model for chemical adsorption is

$$p = f(T)_{\text{adsorbent}} \qquad x_\infty = x_n \tag{8}$$

where n is the mole number of refrigerant adsorbed by the adsorbent.

The change of adsorption quantity in chemical adsorption is stepwise, as shown in Fig. 5, and follows defined equilibrium conditions. Each reaction with defined stoichiometric coefficients is described by one equilibrium condition, and the maximum amount of refrigerant adsorbed cannot be higher than the stoichiomeric value. This implies that, once the system reaches the equilibrium at a certain condition of temperature, the increase of the pressure do not increase the amount of refrigerant adsorbed, unless, the equilibrium condition of other reaction with other stoichiometric coefficients is reached.

5. Adsorption working pairs

5.1. Cycle description

An adsorption cycle comprises four steps divided in two phases: desorption and condensation, evaporation and adsorp-

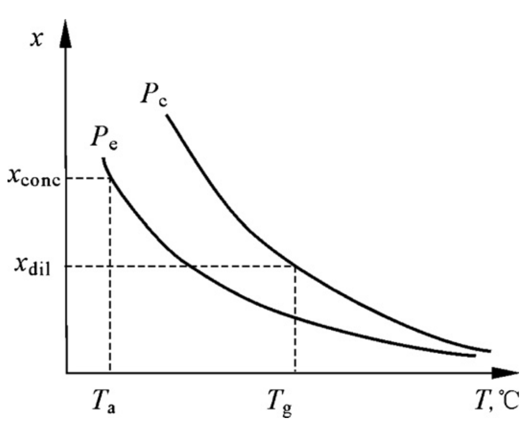

Fig. 4. Equilibrium adsorption/desorption curves under the condition of fixed evaporating pressure and condensing pressure. Adsorption: adsorption temperature T_a, evaporating pressure P_e; desorption: desorption temperature T_g, condensing pressure P_c.

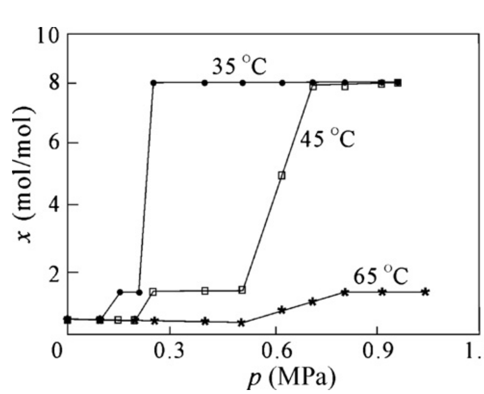

Fig. 5. The adsorption curves of $SrCl_2$–NH_3 working pair [122].

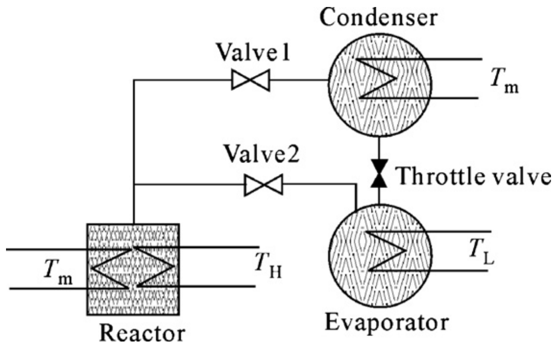

Fig. 6. Basic adsorption refrigeration system.

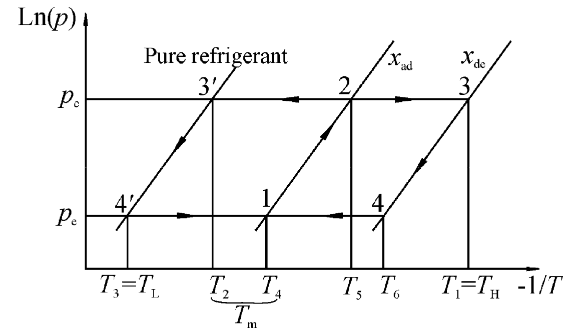

Fig. 7. Adsorption refrigeration cycle (Clapeyron diagram). In adsorber: 1–2, heat input (isosteric heating); 2–3, heat input (isobaric heating and desorption); 3–4, heat rejected (isosteric cooling) 3–4–1, heat rejected (isobaric cooling and adsorption). In evaporator–condensor: 2–3′, heat rejected (isobaric condensation); 3′–4′–1, cooling effect (isosteric refrigerant self-cooling and isobaric evaporation).

tion. In the first phase, an adsorber coupled to a condenser is heated by a heat source at temperature of T_H. The valve 1 (Fig. 6) is opened and the refrigerant vapor flows from the adsorber to the condenser. Theoretically, this phase finishes when the desorption is concluded. At the beginning of the second phase, the valve between the reactor and the condenser is closed. The adsorber is cooled by a heat transfer fluid at T_m and the pressure drops. When the pressure is below the evaporation pressure, the valve that connects to the evaporator and the adsorber is opened, and the adsorption phase starts. The gas consumed by the adsorption is supplied by the evaporation of refrigerant in the evaporator, where cold production occurs at T_L. Theoretically, this phase terminates when the adsorbent in the reactor is saturated.

5.2. Physical adsorption

The adsorption forces involved in physical adsorbents are intermolecular forces (van de Walls force), which mainly include dispersion force, Debye force and orientation force. They do not involve a significant change in the electronic orbital patterns of the species involved. The Clapeyron diagram for physical adsorption working pairs is shown in Fig. 7. The heat and cooling phases are isosteric in ideal processes, and the adsorption and desorption phases are isobaric in ideal processes.

The most studied physical adsorption working pairs are activated carbon (or activated carbon fibre)/methanol [52–58], activated carbon (or activated carbon fibre)/ammonia [59–62], silica gel/water [63–65] and zeolite/water [66–69].

5.2.1. Activated carbon or activated carbon fibre and methanol or ammonia

The adsorption processes of activated carbon/methanol and activated carbon/ammonia are similar, and they comprise filling and condensation of adsorbate inside adsorbent pores. The adsorption mainly occurs in micropores, whose specific volume is generally about 0.15–0.50 $cm^3\,g^{-1}$, and the surface area is about 95% of the whole activated carbon surface area. The function of middle pores and large pores is mainly to transport the adsorbate molecules to micropores.

Activated carbon/methanol is one of the most common working pair due to the large adsorption quantity and lower adsorption heat, which is about 1800–2000 kJ/kg. As the main heat consumption in the desorption phase is due to the adsorption heat, low values of adsorption heat are beneficial to the coefficient of performance (COP, in Eq. (9)). The activated carbon/methanol is also a suitable working pair to use solar energy as heat source due to the low desorption temperature, which is about 100 °C. Temperatures higher than 120 °C should be avoided because according to Hu [58], decomposition of methanol into other compounds occurs above this temperature. However, activated carbon/methanol has the disadvantage of operating under sub-atmospheric pressure. The necessity of vacuum inside a machine using this pair increases the manufacturing complexity, and reduces the reliability of the system, as even a small air infiltration can seriously compromise the machine performance.

$$\mathrm{COP} = \frac{Q_{\mathrm{Cool}}}{Q_{\mathrm{Drive}}} \tag{9}$$

where Q_{Cool} is the cold production, and Q_{Drive} is the heat supplied.

The coefficients of the D–A equation (Eq. (6)) for activated carbon (YKAC, 14–20 mesh, produced from coconut shell) and methanol is [60]:

$$x_0 = 0.45, \qquad k = 13.38, \qquad n = 1.5 \tag{10}$$

Activated carbon/ammonia is another common working pair. Compared with activated carbon/methanol, both pairs have similar adsorption heat, but the former pair had the advantage of higher working pressure, which is about 16 bar at condensation temperature of 40 °C. Due to the higher operation pressure of activated carbon/ammonia pair, the mass transfer performance is better, and the cycle time can be reduced. Other advantage of activated carbon/ammonia pair when compared with activated carbon/methanol pair is the possibility to use heat sources at 200 °C or above. The disadvantages of the activated carbon/ammonia pair is related to the toxicity and pungent odor of ammonia, the incompatibility between ammonia and copper, and the cycle adsorption quantity, which is smaller, when compared to the value obtained with activated carbon/methanol, at the same working conditions. Assuming the activated carbon (YKAC, 14–20 mesh, produced from

coconut shell) studied by Wang et al. [60], the highest adsorption quantity with methanol as refrigerant is 0.45 kg/kg, while with ammonia, it is only 0.29 kg/kg.

The coefficients of D–A equation (Eq. (6)) for activated carbon (YKAC, 14–20 mesh, produced from coconut shell) and ammonia is [60]:

$$x_0 = 0.29; \qquad k = 3.57; \qquad n = 1.38 \tag{11}$$

5.2.2. Silica gel and water

In the adsorption process between water and silica gel, the water molecule is connected with silica alcohol group = Si–OH···OH_2 while the surface coverage degree is low. As the surface coverage degree increases, hydrogen bond becomes the main connecting force. The adsorption heat for this pair is about 2500 kJ/kg and the desorption temperature can be very low, but above 50 °C [23].

There are about 4–6% mass water connected with a single hydroxyl group on the surface of silica atom, which cannot be removed, otherwise the silica gel would lost the adsorption capability. Thus, the desorption temperature cannot be higher than 120 °C, and it is generally lower than 90 °C.

Researchers in Japan developed a three stage adsorption system with silica gel/water working pair, and such a system can be powered by heat sources with temperature of 50 °C [7,63]. The silica gel adsorption chiller developed by Shanghai Jiao Tong University could be powered by a heat source with temperature of 55 °C [70,71]. Such a low desorption temperature is very suitable for solar energy utilization [72].

One disadvantage of silica gel/water working pair is the low adsorption quantity, which is about 0.2 kg/kg. Another disadvantage is the impossibility to produce evaporation temperatures below 0 °C.

The coefficients of D–A equation (Eq. (7)) for silica gel (average particle size of 6 mm, pore size varying between 1.5 nm and 3.0 nm) and water is [51]:

$$n = 1.7, \qquad x_0 = 0.35, \qquad D = 6 \times 10^{-6} \tag{12}$$

5.2.3. Zeolite/water

The structure and adsorption mechanism of different zeolites are different. For example, type A and type X and Y zeolites have the structure of truncated octahedron, and such unit crystals are called as the cage structure of sodalite zeolites. There are 24 water molecules could be adsorbed in the center cages or the pores of unit crystal and in the cages or pores of eight sodalite zeolite crystals. The skeleton structure of type X and Y zeolites is similar to that of natural zeolites. The volume of pores for type X and Y zeolites are larger than the volume of other types of zeolites, and their void ratio can be as high as 50% when there is no water adsorbed. One crystal unit can have 235 molecules of water after adsorption, and most of the molecules would accumulate in the center pore [23].

The zeolite/water pair can be utilized in dehumidification cooling system and adsorption refrigeration system. The adsorption heat for zeolite/water pair is higher than that of silica gel/water pair, and it is about 3300–4200 kJ/kg. The zeolite/water is stable at high temperatures; hence, this pair can be used to recover heat above 200 °C. The adsorption isotherm is quite insensitive to the condensation pressure, thus, the system can operate with similar performance in a large range of condensation temperature. Due to the large adsorption heat and high desorption temperature, the performance of zeolite/water pair is worse than that of activated carbon/methanol pair at middle and low temperature heat sources (lower than 150 °C), but the former pair can have higher COP and SCP if the temperature of the heat source is higher than 200 °C.

The disadvantages of this pair are similar to the disadvantages of the pair silica gel/water: impossibility to produce evaporation temperatures below 0 °C and bad mass transfer performance due to the low working pressure. Due to the high value of adsorption heat and high desorption temperature, for a heat source with same power, the cycle time for the pair zeolite/water is longer than that of other pairs.

The coefficients of D–A equation (Eq. (6)) for zeolite (4–8 mesh, grain diameter of 2.38–4.75 mm) and water is [73]:

$$x_0 = 0.261, \qquad k = 5.36, \qquad n = 1.73 \tag{13}$$

5.3. Chemical adsorption working pairs

For the adsorption between chemical adsorbents and refrigerants, the force of chemical adsorption working pairs are mainly includes the function of complexation, coordination, hydrogenation and oxidization.

The working principle of chemical adsorption is shown in Fig. 8 [74]. Similar to the physical adsorption cycle, the chemical adsorption cycle includes four processes divided into two phases: decomposition, condensation, evaporation and synthesis, which are shown in points 1–4 in Fig. 8.

Chemical adsorption working pairs mainly include metal chlorides/ammonia [25,75–79], metal hydrides/hydrogen [4,80,81] and metal oxides/oxygen [30,82].

5.3.1. Metal chlorides and ammonia

The force between metal chlorides and ammonia is complexation force. The reaction between calcium chloride

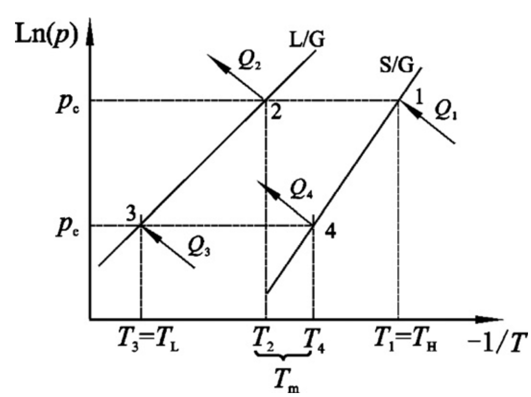

Fig. 8. The Claperon figure of chemical adsorption. Point 1, decomposition (desorption); point 2 condensation; point 3, evaporation; point 4, synthesis (adsorption) [74].

and ammonia can be written as

$$CaCl_2{\cdot}n_1NH_3 + n_2\Delta H_r \leftrightarrow CaCl_2{\cdot}(n_1 - n_2)NH_3 + n_2NH_3 \tag{14}$$

where ΔH_r is the reaction enthalpy (J/mol), the numbers of n_1 and n_2 could be 2, 4 and 8.

The equilibrium pressure for different chlorides is shown in Fig. 9 [83], and the reaction enthalpy (ΔH), reaction entropy (ΔS) and specific heat capacity (C_p), are shown in Table 2.

The advantage of metal chlorides/ammonia is the large adsorption quantity, which is higher than 1 kg/kg for most chlorides.

The disadvantage of metal chlorides/ammonia as working pair is mainly related to the salt swelling and agglomeration during adsorption, which compromise the heat and mass transfer.

5.3.2. Metal hydrides/hydrogen

Similar to the synthesis and decomposition process of chlorides–ammonia, the adsorption and desorption process between metal hydrides and hydrogen depends only on the condition of temperature or pressure. Advanced porous metal hydrides (PMHs), or the misch metal (Mm) matrix alloys, including the alloys with Ni, Fe, La, Al, have very high reaction heat and adsorption quantity.

The disadvantage of metal hydrides/hydrogen working pair is the small SCP (specific cooling power per kilogram of adsorbent). One of the advantages is that the adsorbers are also used as condenser and evaporator. Another advantage of metal hydrides is the large density (ρ = 6.5–8 kg/L), which combined with large adsorption capacity leads to high volumetric cooling capacity. This feature is interesting in situations where the space is limited, but there is no need of lightness.

The basic cycle for metal hydrides/hydrogen working pair is different from that for physical and chemical adsorbents because there is no refrigerant in the saturated state. The principle of a basic cycle is shown in the Van't Hoff diagram of Fig. 10 [84,85]. Eq. (15) is used to calculate the equilibrium

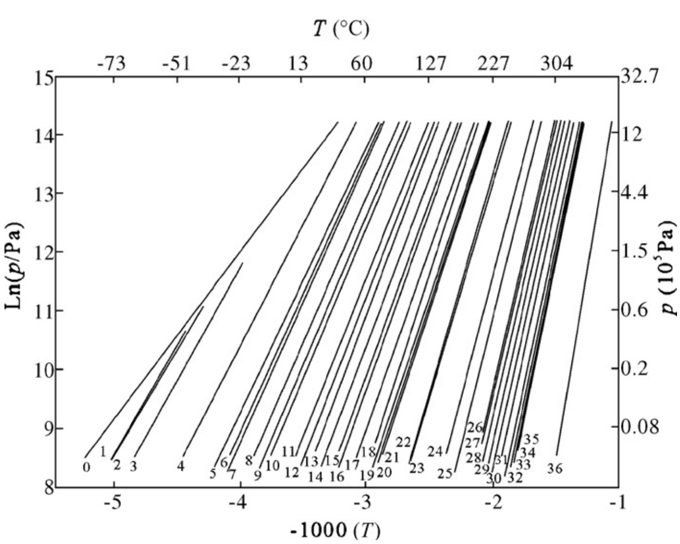

Fig. 9. The equilibrium reaction lines of chlorides [83].

Table 2
Reaction parameters for chlorides/ammonia (corresponding to the reaction equilibrium in Fig. 9) [83]

Number	Reaction material	ΔH (J mol^{-1})	ΔS (J mol^{-1} K^{-1})	C_p (J mol^{-1} K^{-1})
0	NH_3	23,366	150.52	80.27 (liquid)
1	Zn/10-6	29,588	219.23	71.27
2	Cu/10-6	31,387	227.72	71.81
3	Sn/9-4	31,806	224.86	70.60
4	Pb/8-3.25	34,317	223.76	70.05
5	Ba8-0	37,665	227.25	75.10
6	Sn4-2.5	38,920	229.82	70.60
7	Pb3.25-2	39,339	230.27	70.05
8	Ca8-4	41,013	230.30	72.52
9	Sr8-1	41,431	228.80	75.53
10	Ca4-2	42,268	229.92	72.52
11	Zn6-4	44,779	230.24	71.27
12	Pb2-1.5	46,035	230.89	70.05
13	Pb1.5-1	47,290	232.50	70.05
14	Mn6-2	47,416	228.07	72.86
15	Zn4-2	49,467	230.24	71.27
16	Cu5-3.3	50,241	230.75	71.81
17	Fe6-2	51,266	227.99	76.57
18	Cu3.3-2	56,497	237.22	71.81
19	Co6-2	53,986	228.10	78.41
20	Pb1-0	55,660	231.04	70.05
21	Mg6-2	55,660	230.63	71.31
22	Ni6-2	59,217	227.75	71.60
23	Ca2-1	63,193	237.34	72.52
24	Ca1-0	69,052	234.14	72.52
25	Mn2-1	71,019	232.35	72.86
26	Mg2-1	74,911	230.30	71.31
27	Fe2-1	76,167	231.91	76.57
28	Co2-1	78,134	232.17	78.41
29	Ni2-1	79,515	232.17	71.60
30	Zn2-1	80,352	229.72	71.27
31	Mn1-0	84,202	233.18	72.86
32	Fe1-0	86,880	233.01	76.57
33	Mg1-0	87,048	230.88	71.31
34	Co1-0	88,303	232.80	78.41
35	Ni1-0	89,810	233.01	71.60
36	Zn1-0	104,625	227.79	71.27

pressure of hydrides and also of other types of chemical sorbents, such as chlorides reacting with ammonia.

$$R \ln P = \frac{\Delta H}{T} - \Delta S \tag{15}$$

In the first semi-cycle, the metal hydride B desorbs at the temperature of T_{Drive} and the desorbed gas enters the reactor with the metal hydride A. The metal hydride A is cooled by the temperature T_m. The second semi-cycle proceeds at low pressure. The desorption process of metal hydride A absorbs heat and produces cold at the temperature of T_{Cool}. The refrigeration performance is related to the value of the reaction enthalpy. If the system with this pair is used for refrigeration, the COP can be calculated with Eq. (9), while if the system is used as heat pump, the coefficient of amplification (COA) can be calculated with Eq. (17).

$$COA = \frac{Q_{Heat}}{Q_{Drive}} = \frac{Q_{m,A} + Q_{m,B}}{Q_{Drive}} \tag{17}$$

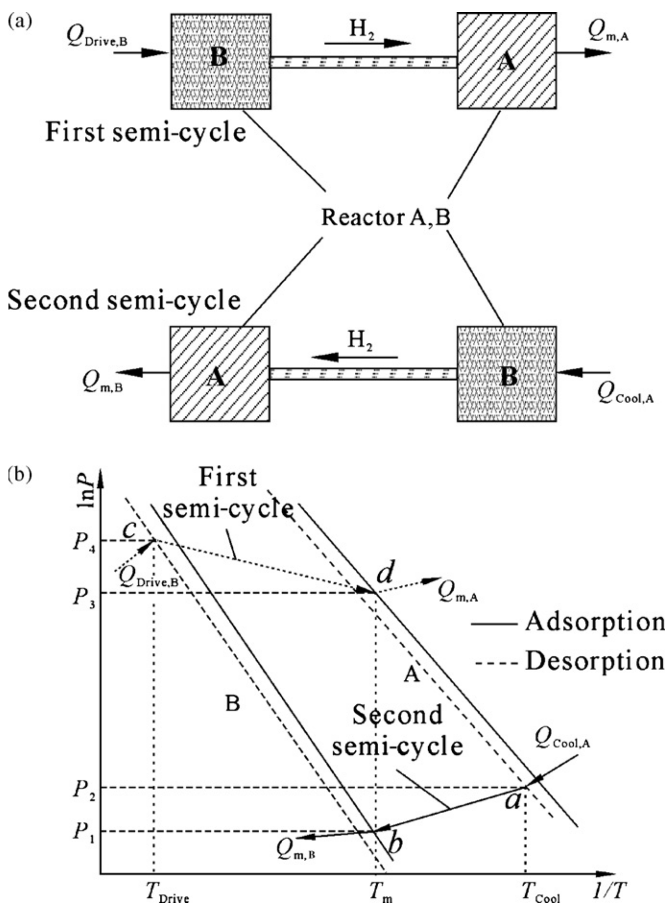

Fig. 10. Working principle of basic cycle and the Van't Hoff diagram [85]. (a) Adsorption principle; (b) Van't Hoff diagram.

Most metal hydrides/hydrogen working pairs have the phenomenon of adsorption hysteresis, and during the transition process between metals and metal hydrides, the pressure increase at different rates, as can be seen in Fig. 11, where x is the quantity of hydrogen desorbed or adsorbed by two reactors [85].

5.3.3. Metal oxides and oxygen

There two types of oxygen, the molecular oxygen and the atomic oxygen, that can be adsorbed by a metal. The oxygen

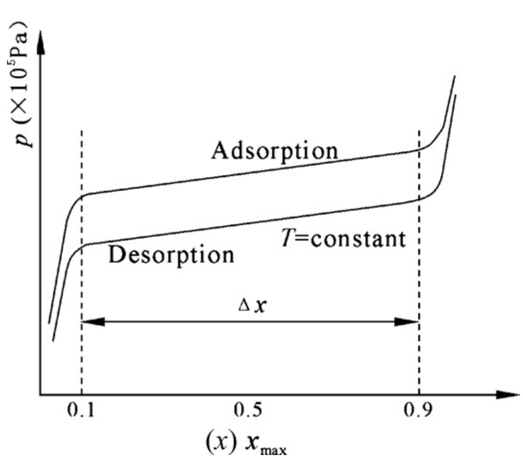

Fig. 11. Adsorption hysteresis phenomenon and pressure slope [85].

atom enters the metal lattice to form metal oxides. The type of oxygen, molecular or atomic, adsorbed by metal depends on the external condition and on the type of metal. Generally, after oxygen molecules are adsorbed, in the heating and desorption process, some oxygen molecules are desorbed, some changed into the stable oxygen atom inside metal, and this transition process needs activated energy [31].

5.4. Composite adsorbents

The main composite adsorption working pairs are silica gel/chlorides/water [86,87] and chlorides/porous media/ammonia [88–90].

5.4.1. Silica gel and chlorides/water

Composite adsorbent with silica gel is mainly produced by addition of chlorides. Chlorides/water working pair, e.g., $CaCl_2/H_2O$, is a not a solid sorption working pair because $CaCl_2$ liquefies after absorbs a certain amount of water, but the highest adsorption quantity of $CaCl_2/H_2O$ is about six times the value obtained with silica gel.

Composite adsorbent of silica gel and chlorides are mainly developed by impregnation process [91–94], where the silica gel is immersed in a salt solution, and then dried.

According to Aristov et al. [95], the adsorption characteristics of silica gel composite adsorbents can be modified by: (1) changing the silica gel pore structure; (2) changing the type of salt and (3) changing the proportion between salt and silica gel.

Regarding the pore structure, when the salt particle is much smaller than the size of the silica gel pore, like in the case of mesopore silica gel, the adsorption characteristic of the salt confined in the pore will be similar to that of the bulk salt, however, if the size of the pore is too small, like in micropore silica gel, the adsorption characteristic can be completely different. Moreover, it is reasonable to expect that silica gel compounds produced with different salts will also present different characteristics.

The proportion between salt and silica gel influences the phenomena of salt swelling and agglomeration, heat transfer and mass transfer of the adsorbent bed. High proportion of salt increases the possibility of salt swelling and salt agglomeration, which spoils refrigerant mass transfer; however, also enhances the heat transfer in the bed.

The adsorption isotherms of silica gel/$CaCl_2$/water pair with different mass ratio of $CaCl_2$ is shown in Fig. 12 [87]. The letter S in the legend, followed by a number, represents the concentration of the salt solution used to make the composite adsorbent. For example, S0 represents silica gel with no salt, and S40 represents the composite adsorbent made with a 40% $CaCl_2$ solution. Fig. 12 shows that the increment in the equilibrium adsorption quantity with the solution concentration decreases when the solution concentration is higher than 40%. As the salt can easily liquefy during the adsorption process when the compound is prepared with a high concentration solution, the best concentration to avoid such a problem and ensure high adsorption capacity would be around 40%.

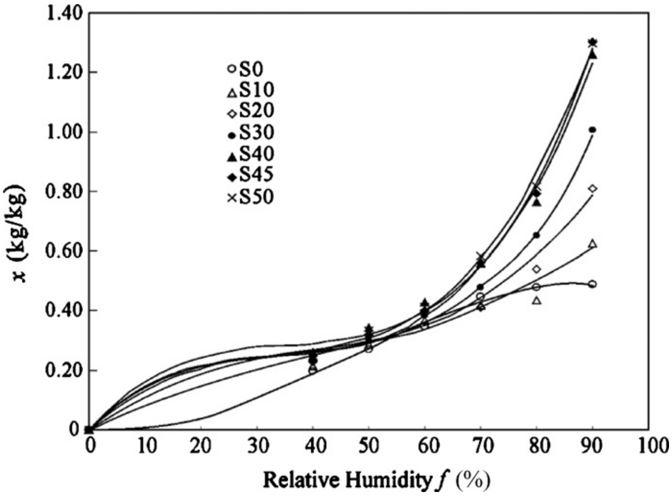

Fig. 12. Isotherms at 40 °C [87].

5.4.2. Chlorides, porous media and ammonia

Four types of porous media are used to produce composite adsorbents with chlorides: expanded graphite, activated carbon, activated carbon fibre and vermiculite.

Expanded graphite is utilized to make composite adsorbents with chlorides, which present enhanced heat transfer and mass transfer properties, and almost no expansion during the adsorption process [96].

Expandable graphite needs to be expanded before it is mixed or impregnated with chlorides. The method is to put the graphite powder in an oven with low temperature for few hours to first remove the humidity of the powder, and then expand the graphite at about 300–700 °C for few minutes to few hours, according to the temperature chosen. The structure of the expandable graphite greatly changes after expansion, and this change can be seen in the scanning electron microscope (SEM) picture shown in Fig. 13 [96].

A composite adsorbent of $CaCl_2$ and expanded graphite called IMPEX, for which the solution of 20 wt% $CaCl_2$ was utilized to impregnate with the graphite block, was developed by the research group of Mauran [19,96–98]. The dimension stability of IMPEX was studied, and results showed that the volume expansion rate wall null if the density of graphite block used to produce composite adsorbent was 156 kg/m^3.

Shanghai Jiao Tong University [90,99] also researched the adsorption performance of composite adsorbents with $CaCl_2$ and expanded graphite, and results showed that SCP as high as $1000\,\mathrm{W/kg_{CaCl_2}}$ can be obtained when the mass ratio between expanded graphite and $CaCl_2$ is 1:1, evaporation temperature is −20 to −10 °C, and the heat sink temperature is 20–30 °C. The overall heat transfer coefficient for this compound was 787 W/(m^2 °C).

Wang et al. [100] developed a composite adsorbent of activated carbon and $CaCl_2$, in order to avoid the salt agglomeration, which compromises the mass transfer of the refrigerant in the sorbent bed. Such a type of adsorbent can also improve the heat transfer performance when it is consolidated.

The advantage of composite adsorbent made with activated carbon, when compared with the composite adsorbent made with activated carbon fibre, is the fact that the salt does not separate from the former and accumulates at the bottom of the adsorber when the compound is prepared as a simple mixture.

A swelling space must be reserved for chemical and some types of composite adsorbent because such adsorbents have the phenomena of swelling and agglomeration. The optimal ratio between swelling space and the space for $CaCl_2$ was studied, and this value is 2:1 for pure $CaCl_2$ whereas it is 1:1 for composite adsorbent with activated carbon as additive, when the heat sink temperature is 28 °C and the evaporating temperature is −10 °C. In this condition of heat sink and evaporation temperature, the volumetric cooling density of the composite adsorbent was 40% higher than that of the single chemical adsorbent [16].

Activated carbon fibre is used in combination with chlorides to enhance the heat transfer in the adsorbent bed. Most of the researches are related to impregnated carbon fibres (ICFs) with $MnCl_2$ and graphite fibres intercalation compounds (GFICs) [36,37].

The ICFs are prepared by putting the activated carbon fibre inside a $MnCl_2$–alcohol solution, and then, removing the solvent. Such type of adsorbent has the advantages of simple method and short production time, which is about 3–4 h. The disadvantage of such type of adsorbent is that $MnCl_2$ is easily separated from the carbon fibres after several cycles of adsorption and desorption, which compromises the adsorption performance.

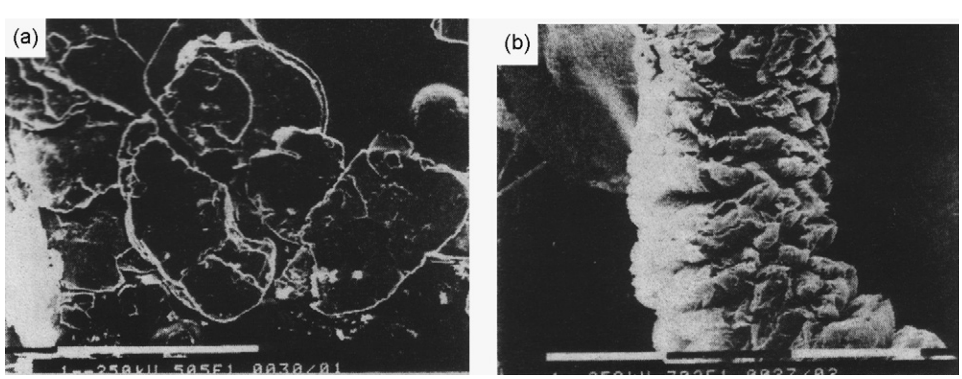

Fig. 13. SEM photo of granular graphite [96]. (a) Before expansion; (b) after expansion.

The method to make GFIC is much more complex than that of ICF. First, the activated carbon fibre is graphitized, and then the $MnCl_2$ needs to be intercalated inside activated carbon fibre in a chlorine atmosphere at 500 °C. Then, small amounts of other salts such as $FeCl_3$ and $CuCl_2$ need to be added in $MnCl_2$ in order to get high rate of intercalation. Such a process takes about 1 week to complete. In the case of GFIC the salt grains are separated at the atomic scale between graphite layers, and even if part of the salt tends to leave the interlayers all the salt adheres perfectly to the fibers.

The optimal adsorption performance of ICF–ammonia is similar to the performance of GFIC–ammonia and this value is 1 kg/kg for the latter and 0.95 kg/kg for the former.

Vasiliev [101,102], also developed a composite adsorbent, which is called Busofit, of activated carbon fibres impregnated with salt, but the solvent was water instead of alcohol. The salt was evenly distributed over the carbon fibre surface as a 2–3 μm film. Such a type of adsorbent is mainly utilized for resorption system using ammonia as refrigerant.

6. Methods to measure adsorption performances

The adsorption quantity needs to be measured under equilibrium and non-equilibrium conditions to assess the maximum amount that can be adsorbed/desorbed under a certain condition, and to assess how long it takes to reach this value. Such studies are essential for the estimation of refrigeration performances. The measurement of the equilibrium adsorption quantity can be done by volumetric, gravimetric and chromatography methods. The adsorption heat is usually measured by calorimetry. Volumetric and gravimetric methods are traditionally used to measure adsorption rate [103], although calorimetry can be also employed. Calorimetry is often utilized to get thermodynamic and kinetic parameters for different adsorption working pairs [104]. The adsorption quantity can be assessed by gas chromatography due to the variation of heat conductivity of the gas with the density, which changes during the adsorption or desorption. However, such a method is rarely used because of its complexity.

In one of the types of volumetric methods, the variation of mass is assessed by measuring the variation of pressure in a vessel with known volume. The measuring principle of this method is shown in Fig. 14 [105]. A thermostatic bath controls the temperature of a saturated fluid located in the generator, and the vapor produced flows towards a storage chamber. A coil water pipe controls the temperature of this chamber. The adsorption and desorption temperature of the adsorbent is controlled by another thermostatic bath. The adsorption quantity is calculated using the values of P_1 and P_2 during adsorption and desorption, respectively, and the value of dead volume of the adsorption equipment. In order to get precise results, the volume of the vapor chamber, the volume of the vapor inside the adsorber, and the mass of adsorbent should be small. The adsorbent mass measured in Fig. 14 was only 3 g [105].

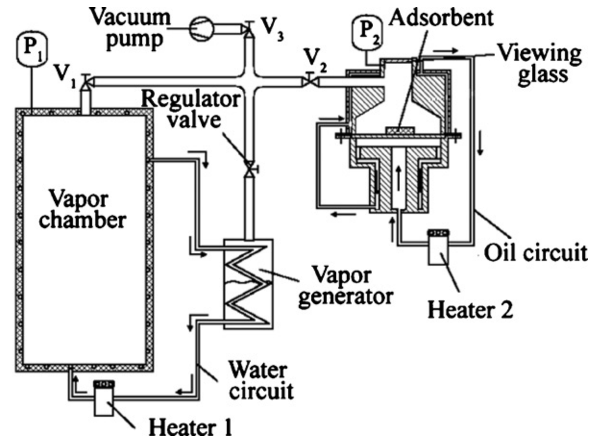

Fig. 14. Test unit for volumetric method [105].

Another type of volumetric method can be used to assess the adsorbed or desorbed mass by measuring the variation of the volume of the refrigerant inside a vessel. The changes in the volume can be identified by measuring the level changes by visual observation or by the utilization of more precise equipments, like magnetostrictive sensor [16,36,100].

A test rig using level sensor is shown in Fig. 15 [36]. In this method, the liquid level in the condenser/evaporator is measured by the level sensor, and this information, together with the value of the useful area of the condenser/evaporator and the density of the refrigerant, is used to calculate the adsorption/desorption quantity. The precision in the measurement increases with the mass of adsorbent, because the amount desorbed/adsorbed, and thus, the variation of the liquid level inside condenser/evaporator also increases.

In the gravimetric method [105], the adsorption performance is calculated by the mass change of the adsorbent during adsorption or desorption. The principle of gravimetric method is shown in Fig. 16 [106]. In the experiments, the length of a quartz spring connected to an empty basket is h_1, and the lengths of quartz spring connected to the basket with adsorbent before and after adsorption, respectively, are h_2 and h_3. Then, the adsorption quantity is

$$x = \frac{h_3 - h_2}{h_2 - h_1} \tag{18}$$

In order to get high precision, the adsorbent mass should be in the order of 0.1–0.3 g [105].

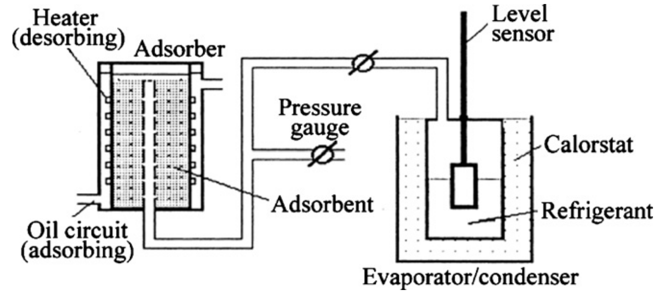

Fig. 15. Test unit for liquid level measuring method [36].

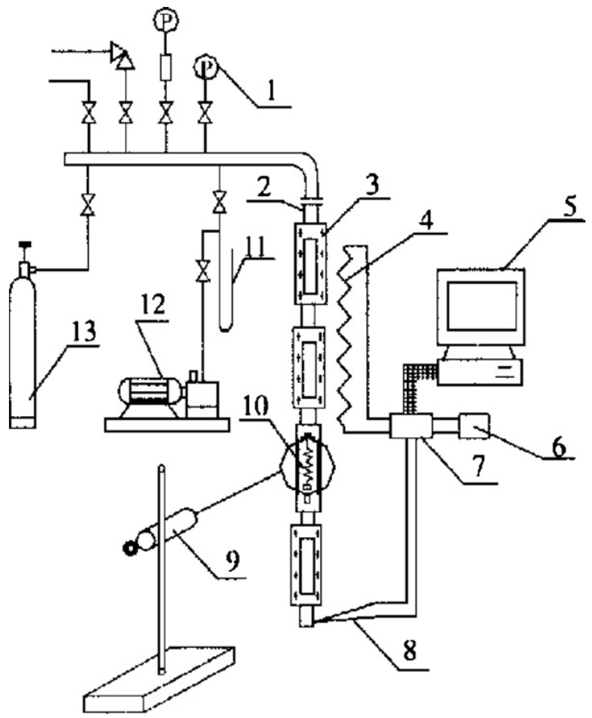

Fig. 16. Test unit for gravimetric method [106]: (1) pressure gauge; (2) measuring tube; (3) viewing glass; (4) electric heater; (5) computer; (6) electric source; (7) temperature controller; (8) thermocouple; (9) altimeter; (10) quartz spring, basket and adsorbent; (11) U shape pressure gauge; (12) vacuum pump; (13) liquid nitrogen cylinder.

The volumetric method that uses the variation of the liquid level to assess the adsorption performance is better than the volumetric method that employs variation of pressure and the gravimetric method described above because of the operation of the equipments involved is easier, the precision is higher, and the test rig is simpler.

Two types of calorimeters can be used to the test adsorption heat: one type is isothermal and the other is adiabatic. The adsorption heat can be assessed in isothermal calorimetry by melting ice or other solid chemical material, such as phenol (melting point of 40.6 °C) or glacial acetic acid (melting point of 16.7 °C), and measuring the mass of the liquid. To ensure high precision in this method, it is important that the amount of liquid produced is much larger than the possible amount of liquid drops that can stay connected to the solid material or to the adsorber wall. This method is not convenient to the measure adsorption equilibrium conditions because each condition would require a different melting material.

In adiabatic calorimetry, the adsorber need to be thermal insulated, and the adsorption heat is calculated using the temperature lift and the thermal capacity of the heat transfer media.

Kinetics of chemical adsorbents can be studied with differential scanning calorimeter and the kinetics of physical adsorbents can be studied with the volumetric method described by Ducourty et al. [107], the gravimetric/calorimetric method described by Smith et al. [108], and the thermogravimetric method described by Henneberg et al. [109].

7. Conclusions and a perspective on adsorption refrigeration pairs

The main heat sources for adsorption machines are waste heat and solar energy. Physical adsorption working pairs are usually preferred when solar energy is the heat source. Silica gel/water is a suitable working pair for solar energy due to the low desorption temperature, but it is can only be applied for the air conditioning due to the impossibility to produce sub-zero temperature.

Activated carbon/methanol pair can be used for freezing applications, and it can be driven by heat sources with temperature lower than 120 °C. Silica gel/water and activated carbon/methanol are also suitable working pairs for low temperature waste heat. Suitable pairs for high temperature waste heat are zeolite/water, activated carbon/ammonia, metal chlorides/ammonia, and composite adsorbents/ammonia. Adsorption refrigeration systems with silica gel/water, activated carbon/methanol and the zeolite/water operate under vacuum, and leak-proof machines are essential to maintain the performance of the system. Systems that utilize ammonia as refrigerant have positive pressure, and the manufacturing and maintenance are much easier, when compared with vacuum systems.

There are two main parameters to evaluate the performance for adsorption refrigeration: COP, and SCP [110]. COP can be improved by advanced adsorption refrigeration cycle, such as heat recovery cycle and mass recovery cycle, and SCP can be improved by advanced adsorber technology and by using adsorbent with high heat and mass transfer performance.

The SCP of different adsorption working pairs are shown in Table 3. The SCP in the table is calculated as follows:

$$\mathrm{SCP} = \frac{W_{\mathrm{L}}}{m_{\mathrm{a}}} \tag{19}$$

where W_{L} is the cooling power for semi-cycle, and m_{a} is the adsorbent mass in one adsorbent bed.

Table 3 [20,70,71,85,99,111–117] shows that some of the promising experimental performances were obtained with composite adsorbents/ammonia working pair. The SCP obtained with the pair activated carbon/$CaCl_2$/ammonia is as high as 731 W/kg and the COP about 0.4–0.5, when the evaporating temperature was −15 °C. However, some calculations indicate that SCP higher than 1000 W/kg can be obtained with convective wave cycle using activated carbon/ammonia working pair and with expanded graphite/$CaCl_2$/ammonia working pair.

The main direction for future research work on adsorption working pairs is related to advanced adsorbent technology with high heat and mass transfer performance. Promising results have been obtained with the composite adsorbents and consolidated adsorbents. However, improvements in heat transfer often results in deployment of the mass transfer performance, thus, research should be focused in producing adsorbent where both mass and heat transfer can be satisfactory. Generally, consolidated adsorbent with high density and short mass transfer path has both good heat and mass transfer

Table 3
Performance comparison of different adsorption working pairs

Evaporating temperature (°C)	Adsorption working pair	COP	SCP (W/kg)	Characteristics	Data source
8	Activated carbon/NH_3		1000	Convective thermal wave cycle	Cal.[a] [111]
1	Activated carbon fiber/$CaCl_2$/NH_3	0.6	330	Composite adsorbent, heat pipe heating	Exp.[b] [20]
3	Activated carbon/NH_3	0.67	557	Convective thermal wave cycle	Cal. [112]
−10	$SrCl_2$–NH_3	0.32	230	Single effect system	Exp. [113]i
−25	($MnCl_2$ + $NiCl_2$)–NH_3	0.4	70 × 2[c]	Double effect system	Cal. [113]
−10	Metal hydride/hydrogen	0.43	25 × 2	Thermal wave cycle	Exp. [85]
3	Graphite/silica gel/water		35 × 2	Composite adsorbent to intensify the heat transfer	Exp. [114]
10	Silica gel/water	0.4	85	Split heat pipe type evaporator	Exp. [70,71]
5	Zeolite/water	0.9	125 × 2	Intermittent convective thermal wave cycle	Cal. [115]
−15	$CaCl_2$/activated carbon/ammonia	0.41	731	Composite adsorbent, heat pipe type heating and cooling	Exp. [116,117]
−25	$CaCl_2$/activated carbon/ammonia	0.36	627.7	Composite adsorbent, heat pipe type heating and cooling	Exp. [116,117]
−15	$CaCl_2$/graphite/ammonia	0.3	1000	Composite adsorbent	Cal. [99]

[a] Cal.: data calculated from the adsorption performances of working pairs or from the simulation of an adsorption refrigeration cycle.
[b] Exp.: data obtained experimentally.
[c] The SCP in the original literature was calculated based on the total cycle time, with adsorption and desorption of same length. To allow a fair comparison, the original value should be multiplied by two.

performance, however, the increase of the volume occupied by the mass transfer channels reduces the amount of the adsorbent that can be placed in a specific space.

Another direction for future research work is the search for working pairs that could be powered by low temperature and could be utilized to obtain temperatures below −10 °C. At this level of temperature and below, physical adsorption working pairs such as activated carbon/methanol and activated carbon/ammonia can only adsorb small quantities of 0.05 kg/kg or even lower, if the condensation temperature is 25 °C, and the heat source temperature is about 100 °C [60]. Chemical adsorbents such as calcium chloride also do not produce good performance when the driven heat source temperature is lower than 100 °C [100]. Ammoniates of $BaCl_2$ can desorb quickly at temperatures between 60 and 80 °C [101], but they cannot achieve temperatures lower than −10 °C if the heat sink temperature is higher than 20 °C, and therefore, they cannot be used to produce ice in the summer.

The main problem on the adsorption refrigeration research nowadays is the kinetic research of chemical and composite adsorption refrigeration. For the composite adsorption which utilizes graphite as additive, several kinetic models have be established and tested, and the first model based on the assumption that the reactive medium was uniform in temperature, pressure and composition was developed by Lebrun and Spinner [118]. Then an experimental study in which pressure in the macropores of the medium was measured and found to be quasi-uniform, brought to light the existence of strong temperature gradients in the reactive medium. Mazet et al. developed an adapted procedure in which identification of the kinetic and thermal parameters was separated [119]. The phenomenological model, which utilized the concept of the grain–pellet is also studied by Goetz and Marty [120], and it is useful because it makes it possible to define two characteristic dimensions in the reactive medium: the grain, which is the basic particle where the reaction takes place and the porous solid matrix (the pellet), which is composed of a combination of reactive particle with or without the presence of an inert binder. For the composite adsorbent of chlorides which utilizes activated carbon and silica gel as additive, researches found that the adsorption process is not only influenced by the heat and mass transfer process inside porous media, the chemical reaction between chemical adsorbent and refrigerant, but also is influenced by the physical adsorption process of activated carbon or silica gel, which makes the kinetic analysis much more complex [65,86,121].

Another problem for the simulation of adsorption performances for chemical and composite adsorption working pairs is the heat and mass transfer process. The heat and mass transfer performances of adsorbent change in the process of adsorption and desorption for the reason of swelling and agglomeration processes, and the heat and mass transfer performances are also different while the volume filling ratio of adsorbent is different inside the reactor because the density changes. For the heat conductivity measurement under such a condition, the internal heat source exists for the reason of the adsorption heat and desorption heat in the process of adsorption and desorption, and the heat conductive media, such as refrigerant vapor also exists in the reactor, thus the traditional hot-wire measurement method, which requires no internal heat source and no heat conductive media, cannot be utilized. The transient plane heat source (TPS) technology is proposed for the heat conductivity measurement. This method has the problem of that the plane sensor is easier to be distorted by the force of expansion for chemical and composite adsorbents. Meanwhile, to find an effective method to measure the mass transfer performance at the different adsorption quantity is also essential for the precise prediction of adsorption refrigeration performance for chemical and composite adsorption working pairs.

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